

Effect of Coal Ash on the Steam Reforming of Simulated Bio-oil for Hydrogen Production over Ni/ γ -Al₂O₃

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An improved system for hydrogen production by the steam reforming of simulated bio-oil was developed. The coal ash was packed in front of nickel-based catalysts, acting as a guard catalyst. The model compounds passed through coal ash and were preliminarily reformed to smaller molecular intermediates containing more CO and CH₄, which were then further reformed over the following nickel-reforming catalyst. The improved reaction system succeeded in effectively converting the complex simulated bio-oil into hydrogen and exhibited high activity. For 15 wt.% Ni/ γ -Al₂O₃ catalyst with coal ash packing, the catalyst lifetime was extended to 8 h, with simulated bio-oil almost completely converted into hydrogen. In addition, coke deposition was suppressed.

Keywords: Hydrogen; Bio-oil; Steam reforming; Coal ash; Guard

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INTRODUCTION

Fossil fuel depletion and the environmental crisis are two important issues that require attention around the world. Clean and renewable energy has therefore drawn increasing attention. Biomass is the sole renewable energy resource that contains carbon, which can be converted into liquid fuel as an alternative to fossil fuel (Huber *et al.* 2006). Through pyrolysis, solid biomass can be converted into easily transported liquid fuel, known as bio-oil. Bio-char and uncondensed gases are two of its byproducts. Bio-oil is known as a promising drop-in fuel. However, considering its relatively low heating value, thermal sensitivity, and high water content, raw bio-oil must be upgraded by hydro-processing (Zhao *et al.* 2009) and cracking (Wang *et al.* 2014b) to become a qualified transport fuel. In this case, the direct upgrading of raw bio-oil at a low H/C_{eff} ratio often leads to low activity and rapid catalyst deactivation in the presence of large oxygenated molecular compounds (Vispute *et al.* 2010). Similarly, it has been reported that severe coke deposition occurs during the initial decomposing stage when bio-oil vapor is in direct contact with a Ni/Al₂O₃ catalyst (Davidian *et al.* 2007). With an increase in the H/C_{eff} ratio, the upgrading activity is remarkably enhanced and the deposition of coke is significantly inhibited (Zhang *et al.* 2011). Thus, a large amount of hydrogen is required to enhance the H/C_{eff} ratio of raw bio-oil to remove the unstable oxygenated compounds.

It is worth noting that the unstable oxygenated compounds could be removed by the steam-reforming of acids and aldehydes, *etc.*, in raw bio-oil. In addition, the steam reforming of bio-oil produces hydrogen, which can in turn be used for upgrading bio-oil itself. The steam reforming reaction at high temperatures encounters similar problems, such as coke deposition and catalyst deactivation (Trane *et al.* 2012), as well as high energy consumption. Catalyst activity is severely inhibited by heavy compounds such as sugars

and oligomeric phenols, *etc.*, in raw bio-oil (Trimm 1997). Therefore, bio-oil is frequently pretreated by adding water to form an aqueous phase (Wang *et al.* 1998; Garcia *et al.* 2000; Bimbela *et al.* 2011; Remón *et al.* 2013) or gathering active volatiles (Wang *et al.* 2007; Valle *et al.* 2014). In this way, the inactive components in bio-oil are left behind, including pyrolysis lignin. Apart from the aqueous phase and volatiles, bio-oil has been proposed to be separated by molecular distillation, operated under mild conditions to retain its major components (Wang *et al.* 2009, 2015b). Two fractions can be obtained *via* molecular distillation: a light distilled fraction enriched with water and small-molecular weight oxides and a heavy residue fraction enriched with large-molecular weight oxides. The light distilled fraction of bio-oil can be converted easily (Wang *et al.* 2014b). By using its light distilled fraction rather than the raw bio-oil, hydrogen can be obtained by steam reforming this water-rich fraction and can then supply the hydrogen required in the hydroprocessing of bio-oil, as proposed above (Wang *et al.* 2013). In addition to reactant treatments, in recent years, many studies have been devoted to develop more active and stable steam reforming schemes (Wu *et al.* 2008; Wu and Williams 2009; Lónyi *et al.* 2013; Ren *et al.* 2014) in comparison with the conventional single-stage fixed bed reactor. van Rossum *et al.* (2007) placed a sand fluidized bed before a fixed catalytic bed to combine the atomization/cracking of the oil and the catalytic steam reforming of the produced gases. The results showed that the catalyst was successfully protected and the energy efficiency was improved. Ma *et al.* (2014) proposed a novel process integrating pyrolysis, gas-solid simultaneous gasification with subsequent reforming to improve hydrogen yield, mostly by converting char and hydrocarbon to syngas. Kan *et al.* (2010) introduced quartz into the catalyst bed to facilitate bio-oil's decomposition first into smaller intermediates, which then passed through the following steam-reforming catalyst. In this way, the catalyst lifetime was improved by the inhibition of coke deposition. Additionally, by the simple dilution of quartz, dolomite as the so-called guard catalyst was also used ahead of catalysts to protect the latter catalyst from extensive contact with the reactant, improving bio-oil conversion (Lónyi *et al.* 2013). Therefore, the direct catalytic steam reforming of bio-oil with a guard layer addition in the bed is a promising technology.

Coal ash, one of the main contributors of solid waste in power plants, is thermally stable and difficult to dispose of. In recent decades, it has been explored for several applications in catalytic processing, the construction industry, adsorbents, ceramics and glass, concrete, *etc.* (Blissett and Rowson 2012). In addition to its physical properties, coal ash has also drawn attention because of its chemical features. Because coal ash contains many alkali and alkaline earth metals (AAEM) as well as some iron, it has been shown to be active in catalytic processes. Zeng *et al.* (2014) prepared an effective Brønsted solid acid from coal ash and found that it had high catalytic activity and stability in the production of dimethyl ether from the methanol dehydration reaction. Muhammad *et al.* (2012) employed coal ash as a support to prepare Co-based catalysts for phenol degradation, and these catalysts showed higher activities than Co catalysts. In the steam reforming of bio-oil compounds, nickel supported on coal ash also exhibited high catalytic activity for hydrogen production (Wang *et al.* 2014c, 2015a). Nowadays globally, approximately 750 million tons of coal ash is generated annually, while the utilization fraction is only 25% (Wang 2008; Blissett and Rowson 2012). Although coal ash has been used as a catalyst support, few reports have focused on its direct catalyst performance. Herein, coal ash was selected to function as a guard catalyst in the steam reforming of bio-oil for hydrogen production.

EXPERIMENTAL

Catalyst Preparation

Ni/ γ -Al₂O₃ catalysts with 5, 10, and 15 wt.% nickel loadings were prepared by wet impregnation. Ten grams of γ -Al₂O₃ (Sinopharm Chemical Reagent Co., China) beforehand ground to powder was added to 100 mL of an ethanol solution of Ni(NO₃)₂ (Sinopharm Chemical Reagent Co.) with a specific concentration. The suspension was stirred for at least 2 h at room temperature, followed by evaporation at 80 °C with continuous stirring. The samples were then dried at 110 °C overnight before being calcined for 2 h at 815 °C. The prepared catalysts were then crushed and sieved to a size of 40 to 60-mesh.

Coal ash was generated from a typical coal (produced in ZhunDong, China) by a standard coal ash manufacturing process (GB/T 1574 (2007)), and was designated as ZDA (ZhunDong Ash). In detail, no more than 0.15 g/cm² coal ash was at first placed in a crucible, and the crucible was then heated to 500 °C for 30 min and kept at 500 °C for 30 min. After that, the temperature was further increased to 815 °C and remained there for 2 h. After cooling, the coal ash was ground to a powder (smaller than 0.1 mm) and once again calcined at 815 °C for 30 min to achieve a constant weight. Prior to the reactions, the coal ash after tableting was crushed and sieved to a size of 40 to 60-mesh. In our previous work, the selected coal ash named ZDA was studied as a catalyst support in acetic acid reforming (Wang *et al.* 2015a).

In the following text, “xNi (x = 5, 10, and 15)” is used to refer to the Ni/ γ -Al₂O₃ catalyst with Ni loading amounts of “x (x = 5, 10, and 15).”

Catalyst Characterization

The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of fresh Ni/ γ -Al₂O₃ catalysts was measured by N₂ physical adsorption. N₂ adsorption-desorption isotherms were recorded at 77 K using a Quadrasorb SI apparatus (Quantachrome, USA). Before this measurement, the sample was degassed at 573 K for 3 h. Powder X-ray diffraction (XRD) analysis was carried out on a D/max-Ra X-ray diffractometer (PANalytical, Holland) with a Cu K α radiation source, operating at 40 kV and 30 mA. Thermogravimetric analysis (TGA) was conducted on a TGA/SDTA851e apparatus (Mettler-Toledo, Switzerland) to study the deposition of carbon onto the catalysts. Each test was conducted in an air flow (30 mL/min) from ambient temperature to 800 °C at 20 °C/min.

Catalytic Activity Test

The catalytic reforming reaction was carried out in a fixed-bed reactor, as shown in Fig. 1. In each experiment, 0.5 g of Ni/ γ -Al₂O₃ catalyst was placed in a quartz tube with an inner diameter of 8 mm. For the improved scheme, 0.5 g of coal ash was placed above the Ni/ γ -Al₂O₃ catalyst acting as the guard catalyst with silica wool separating them into two parts. Before each experiment, the catalysts were reduced with H₂ at 800 °C for 2 h. To have a better understanding of the steam reforming reaction, the model compounds for major chemical groups in raw bio-oil were selected, and their percentages are based on real bio oil produced in our lab and listed in Table 1 (Li *et al.* 2012). The reaction conditions were as follows: reaction temperature 700 °C, steam to carbon molecular ratio (S/C) 9.2, and feed rate 0.2 mL/min.

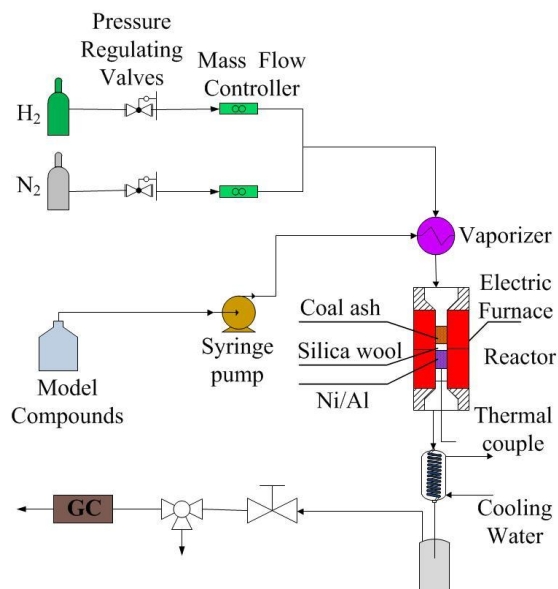
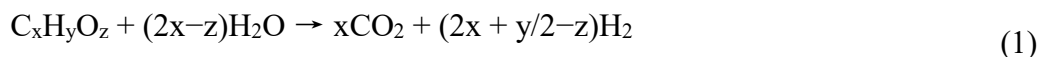


Fig. 1. Bio-oil steam reforming reactor

The overall reforming reaction of bio-oil is shown in Eq. 1, the stoichiometric yield (% stoi.) of H₂ is shown in Eq. 2, and carbon conversion is defined by Eq. 3:



$$H_2 \text{ yield (stoi)} = \frac{\text{moles of } H_2 \text{ obtained}}{\text{moles of } H_2 \text{ in stoi potential}} \times 100\% \quad (2)$$

$$\text{Carbon Conversion} = \frac{\text{moles of C in the outlet gases}}{\text{moles of C in the feed}} \times 100\% \quad (3)$$

Table 1. The Chemical Composition of Simulated Bio-Oil

Component	Content (wt. %)
Methanol	6
Ethanol	4
Acetic acid	25
Hydroxyacetone	4
Furfural	20
Phenol	6
Water	35

RESULTS AND DISCUSSION

Catalyst Characterization

The specific surface area, pore volume, and average pore size of the Ni/ γ -Al₂O₃ catalysts and ZDA are summarized in Table 2, and the N₂ adsorption–desorption isotherms of the fresh catalysts are shown in Fig. 2. For fresh Ni/ γ -Al₂O₃ catalysts, the specific surface areas ranged from 107.8 to 117.8 m²/g. Additionally, a type IV Langmuir adsorption isotherm was revealed (referring to the IUPAC classification) for all Ni/ γ -Al₂O₃ catalysts.

The pore volume was between 0.32 and 0.39 cm³/g for Ni/ γ -Al₂O₃ catalysts. Both the surface area and pore volume decreased with an increase in Ni loading. Compared with the Ni/ γ -Al₂O₃ catalysts, the specific surface and pore volume of ZDA were quite low. The pore detected in the ZDA was probably caused by the particle packing rather than the internal pores, which can be confirmed by its pore volume of almost zero. The pore diameter distributions were presented in Fig. 2, and it could be found that 5 wt.% Ni/ γ -Al₂O₃ catalyst showed a relatively larger main pore size compared with 10 and 15 wt.% Ni/ γ -Al₂O₃ catalysts, in accordance with Table 2.

Table 2. Physical Properties of Ni/ γ -Al₂O₃ Catalysts

Catalyst	SBET (m ² ·g ⁻¹)	Pore Volume (cm ³ ·g ⁻¹)	Average Pore Size (nm)
5 wt. % Ni/ γ -Al ₂ O ₃	117.8	0.39	13.25
10 wt. % Ni/ γ -Al ₂ O ₃	115.9	0.33	11.34
15 wt. % Ni/ γ -Al ₂ O ₃	107.8	0.32	11.87
ZDA (Wang <i>et al.</i> 2015a)	3.55	0.02	29.9

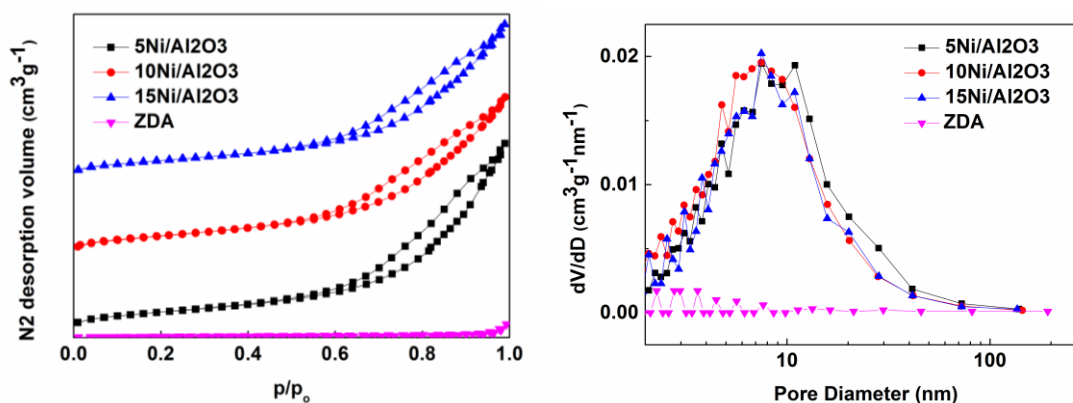


Fig. 2. N₂ adsorption-desorption isotherms and pore size distributions of Ni/ γ -Al₂O₃ catalysts and ZDA

XRD patterns are presented in Fig. 3. A NiAl₂O₄ spinel phase was present in all Ni/ γ -Al₂O₃ samples, indicating a strong interaction between the NiO and γ -Al₂O₃ support when the catalysts were calcined at high temperatures. The main peaks at 37.3, 45.4, and 66.3° were more likely to be assigned to the NiAl₂O₄ phase (37.0, 45.0, 65.5°; JCPD 10-0339) rather than the NiO phase (37.2, 43.3, 62.9°; JCPD 44-1159). The patterns were quite similar because of consistent preparation procedures. There could also be a NiO phase formed but not detected in addition to the NiAl₂O₄ spinel phase, which was reported (Zhao *et al.* 2012).

As the loading increased from 5 to 15 wt. %, the NiAl₂O₄ peaks became narrower; this indicated a larger crystal size, which were measured to be 4.46, 4.72, and 5.05 nm for 5, 10, and 15 wt.% Ni catalysts according to the Scherrer formula, respectively. Typical crystals such as quartz and anhydrite are shown in the XRD pattern of ZDA (Wang *et al.* 2015a).

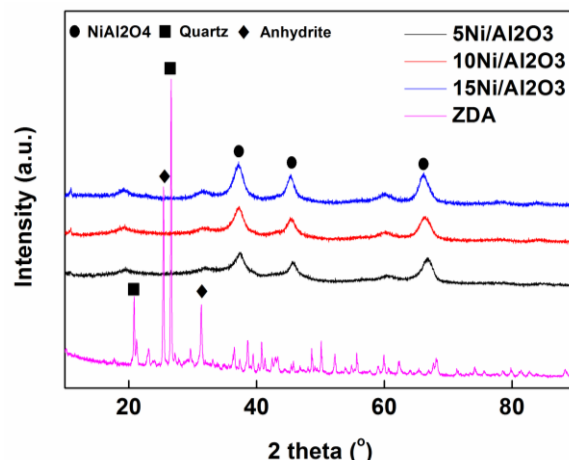


Fig. 3. XRD patterns of Ni/ γ -Al₂O₃ catalysts and ZDA

The features of ZDA were systematically characterized, including chemical composition, surface morphology observed by scanning electron microscopy (SEM), hydrogen temperature programmed reduction (H₂-TPR), and powder X-ray diffraction patterns from our earlier research (Wang *et al.* 2015a). In brief, the coal ash (ZDA) mostly contained SiO₂, Al₂O₃, Fe₂O₃, and various alkali and alkaline earth metals, such as MgO and CaO. The elements were expressed in the form of oxides. The amount of SiO₂ plus Al₂O₃ accounted for approximately 20 wt.%, and that of AAEM was approximately 45 wt.%. With respect to surface morphology, chips were observed, which did not favor porous structures.

Coal Ash Activity

The reforming activity of coal ash itself was analyzed and compared with that of quartz, as shown in Fig. 4. It can be seen that the rate of carbon conversion largely increased from 7.0% to 33.3% and that hydrogen yield increased from 0.9% to 11.9%. As presented, more gaseous products were obtained over ZDA, including CO, CH₄, CO₂, C₂H₄, and C₂H₆. For quartz, simulated bio-oil underwent thermal decomposition and a small amount of carbonaceous gases, such as CO, CH₄, and CO₂, were formed. Similar results were observed in other studies, in which bio-oil rarely produced hydrogen from direct decomposition (Constantinou *et al.* 2010; Liu *et al.* 2012; Remón *et al.* 2014). The hydrogen yield at 0.9% could be attributed to the reactants' direct thermal decomposition.

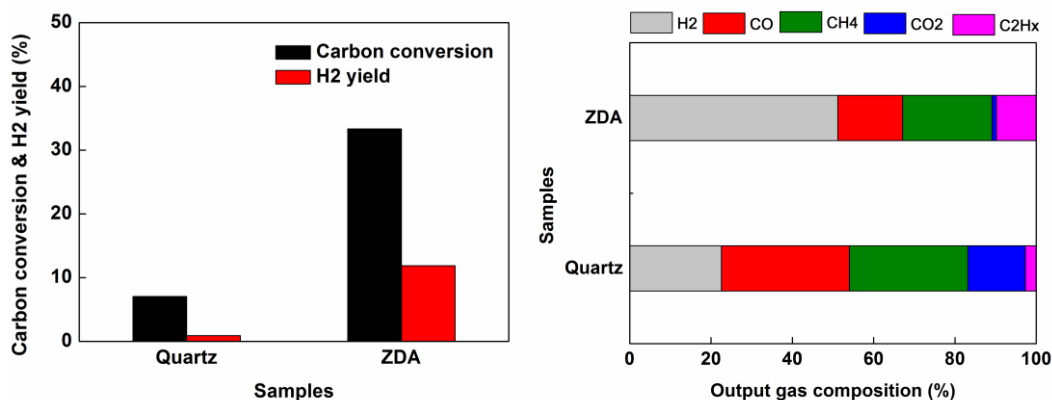


Fig. 4. Reforming of bio-oil over Quartz and ZDA. $T = 700$ °C, LHSV = 12 h⁻¹, S/C = 9.2

The activity of ZDA was confirmed in promoting the conversion of simulated bio-oil into gaseous products (Wang *et al.* 2015a). Iron helped to break C-C bonds (Hu and Lu 2010), while AAEM favored water adsorption (Garcia *et al.* 2000), which can inhibit the polymerization of carbonaceous samples and coke deposition. Under the present conditions, a proportion of feedstock was converted to carbonaceous gases, with CO and CH₄ yields both reaching more than 5%, and hydrogen yield was also improved. In addition, the yields of C₂H₄ and C₂H₆ were obviously enhanced, which were hardly found over quartz. The promotion of bio-oil decomposition was also reported over dolomite, with which more gaseous products such as CO and CH₄ were obtained (Wu *et al.* 2008). However, it was found that CO₂, the major product of reforming reactions, was hardly found in the output gases, which can be ascribed to a quite limited water gas shift reaction.

Guardian Effect of Coal Ash on Bio-oil Steam Reforming

As mentioned above, ZDA converted reactants into gaseous products to a certain degree, similar to the function of quartz and dolomite in a two-stage reaction system (Lónyi *et al.* 2013). In this case, it was utilized as the guard catalyst to primarily steam reform the complex model compounds to H₂, CO, and other smaller molecular intermediates for further reforming reaction. The catalytic activity test was performed over a series of Ni/ γ -Al₂O₃ catalysts, with or without the combination of ZDA. The catalyst performances were obtained from average values after 10 h tests.

As presented in Fig. 5, for the 5 wt.% Ni/ γ -Al₂O₃ catalyst, the carbon conversion and hydrogen yield reached 32.2% and 28.8%, respectively. That is, only a small proportion of bio-oil was converted to carbonaceous gases such as CO, CH₄, and CO₂, which would be further steam-reformed to produce hydrogen. It was observed that the loaded 5 wt.% Ni active metal contributed to a higher hydrogen yield compared with ZDA and quartz, while a large proportion of feedstock was still not converted to hydrogen. Commonly, reactants would go through adsorption, catalytic reaction, and desorption stages. Specifically, when bio-oil vapor made direct contact with the Ni/ γ -Al₂O₃ catalysts, the reactant was at first adsorbed on the γ -Al₂O₃ support surface and then diffused on the Ni active sites to react with water. It can be seen in Table 1 that the major components in simulated bio-oil were acetic acid and furfural. It has been reported that the ketonization reaction dominates when acetic acid molecules are adsorbed on the γ -Al₂O₃ surface, which does not favor hydrogen production (Basagiannis and Verykios 2006). In addition, the other major component, furfural, was quite thermally unstable (Wang *et al.* 2013) and the condensation reaction tended to occur, leading to low conversion over the Ni/ γ -Al₂O₃ catalyst (Sayas and Chica 2014). Under this condition, over 5 wt.% Ni/ γ -Al₂O₃ catalysts, the Ni active sites were not sufficient and could only catalytically convert a small proportion of the reactant for hydrogen production, while the rest reactant tended to undergo thermal cracking or decomposition. A similar case was also observed in that the insufficient 5 wt. % Ni/ γ -Al₂O₃ catalyst led to inadequate activity (Wang *et al.* 2014a).

After loading ZDA prior to the Ni/ γ -Al₂O₃ catalyst, direct contact between the bio-oil vapor and the Ni/ γ -Al₂O₃ catalysts was avoided. The CO and CH₄ yields increased to 16.1% and 17.9%, respectively, causing the overall carbon conversion rate to increase from 32.2% to 64.4%. However, the H₂ and CO₂ yields almost did not change, indicating that the guard catalyst ZDA only preliminarily reformed simulated bio-oil to CO, CH₄, and other intermediates rather than performing like Ni active sites in producing H₂. That is, in the first stage, the guard catalyst ZDA helped to enhance the reactant conversion to more CO, CH₄, and C₂H_x (as was observed in Fig. 4), which could be then further reformed to

produce H₂ and CO₂ over Ni sites in the second stage (Wu and Williams 2009). Because the number of Ni sites was not increased in the latter stage, the reforming degree of CO, CH₄, and C₂H_x to H₂ and CO₂ remained almost unchanged, coupled with more CO and CH₄ left unconverted, leading to a similar hydrogen yield.

It has been revealed that catalytic activity is not promoted when quartz is introduced (Kan *et al.* 2010; Ren *et al.* 2014). At this time, for the selected coal ash (ZDA), the gaseous products were changed, which can be ascribed to the components in ZDA, such as Fe₂O₃, MgO, and CaO. When acetic acid met ZDA under similar reaction conditions, more CH₄ was produced (Wang *et al.* 2015a). Similarly, the activity was enhanced with the aid of ZDA addition over the 5 wt.% Ni/ γ -Al₂O₃ catalyst.

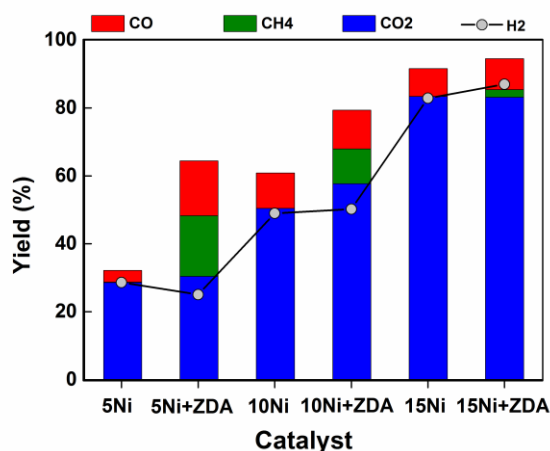


Fig. 5. Catalytic performances of 5, 10, and 15 wt.% Ni/ γ -Al₂O₃ with and without ZDA. $T = 700\text{ }^{\circ}\text{C}$, LHSV = 24 h^{-1} , S/C = 9.2

As the Ni loading amount continually increased to 10 wt.%, the results of the Ni/ γ -Al₂O₃ catalyst with and without ZDA are shown in Fig. 5. Both the CO and CO₂ yields largely increased compared with the 5 wt.% Ni/ γ -Al₂O₃ catalyst because of the increase in loading Ni active sites, causing the whole carbon conversion rate to increase from 32.2% to 60.9% and the H₂ yield to increase from 28.8% to 49.1%. In addition to the improved activity, the carbonaceous gas product distribution did not change significantly. After loading ZDA, the carbon conversion increased from 60.9% to 79.3% while the hydrogen yield almost remained unchanged once again from 49.1% to 50.3%. In addition, the CH₄ yield increased from nearly 0 to 10.2%, with more CO and CO₂ detected.

For the 15 wt.% Ni/ γ -Al₂O₃ catalyst, both the carbon conversion and hydrogen yield were enhanced to a large degree compared with 5 and 10 wt. % Ni/ γ -Al₂O₃ catalysts. With 15 wt.% Ni loading amount, the carbon conversion achieved 91.6%, with a hydrogen yield of 82.7%. After loading the coal ash ZDA, the carbon conversion was further increased to 94.7% and the hydrogen yield increased to 86.8%, with more CH₄ produced. This suggested that a desirable conversion rate of simulated bio-oil to hydrogen was achieved over the 15 wt.% Ni/ γ -Al₂O₃ catalyst in the aid of coal ash ZDA as a guard catalyst.

Effect of S/C on the two-staged Bio-oil Steam Reforming

The performance of the 15 wt.% Ni/ γ -Al₂O₃ catalyst with ZDA at different S/C was investigated as shown in Fig. 6. At a S/C = 7.5, the carbon conversion and hydrogen yield

decreased to 68.4% and 41.2%, respectively. It could be found that the lower carbon conversion and hydrogen yield were caused by a larger amount of CH₄. When the S/C further went down to 5, a rapid decrease of carbon conversion and hydrogen yield were continuously found. The carbon conversion reached only 44.9% and the hydrogen yield 14.4%. CO and CH₄ became the major gaseous products rather than CO₂. This indicated that a high S/C ratio at 9.2 was essential at the high LHSV = 24 h⁻¹.

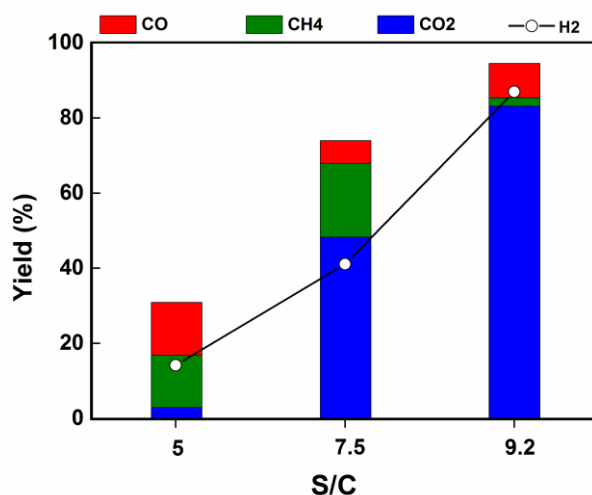


Fig. 6. Catalytic performances of 15 wt.% Ni/γ-Al₂O₃ with ZDA. $T = 700\text{ }^{\circ}\text{C}$, LHSV = 24 h⁻¹, S/C = 5, 7.5, and 9.2

Stability Test of 15 wt.% Ni/γ-Al₂O₃ Catalyst with Coal Ash

The performance of the 15 wt.% Ni/γ-Al₂O₃ catalyst with and without ZDA for the duration of 8 h is presented in Fig. 7. For the 15 wt.% Ni/γ-Al₂O₃ catalyst (Fig. 7(a)), carbon conversion and hydrogen yield achieved 100% and 90% in 2 h, respectively. The 2 h induction time was needed for the catalyst to reach a stably active form during the contact with reactants. In addition, there was a large dead volume between the reactor and gas chromatograph, so the induction period would be longer since the product gases would initially mix up with the residue pure N₂ in the dead volume. Therefore, the lower conversion and hydrogen yield were obtained until the residue N₂ was totally cleared. The highly active performance could be explained by the existence of sufficient Ni active sites on the catalyst for the reforming reaction, as was observed in Fig. 5. The reaction activity was maintained for approximately 6 h and the output gas composition also remained basically unchanged, except for lower carbon conversion and lower H₂ production. Usually, bio-oil is first steam-reformed into CO and H₂. After this, CO would then go through water gas shift reactions to be further converted into CO₂ and produce more H₂. According to Fig. 7(a), after 5 to 6 h, the CO₂ yield decreased slightly, while the yield of CO remained stable, which was probably caused by the Ni active sites starting to gradually lose activity. As was illustrated, after that, both the carbon conversion and hydrogen yield decreased sharply, to 55.0% and 43.0%, respectively. This could be attributed to the catalyst deactivation, which was caused by coke deposition and/or metal sintering. The coke deposition and/or metal sintering decreased the metal surface accessible to reactants (Bengaard *et al.* 2002). The catalysts adopted in bio-oil reforming have been frequently reported to suffer rapid deactivation (less than 1 h (Kan *et al.* 2010) or 6 h (Fu *et al.* 2014)). Considering the large amounts of acetic acid and furfural in the bio oil compounds, the

coke deposition and catalyst deactivation were reasonable. It has been frequently reported that the steam reforming of acetic acid over alumina supported Ni favored carbon deposition due to the acid property of alumina together with acetic acid ketonization reaction (Basagiannis and Verykios 2007; An *et al.* 2011). Furfural was a cyclic model compound containing a carbonyl group, which tended to undergo self-condensation reactions leading to carbon deposition and catalyst deactivation (Trane-Restrup and Jensen 2015).

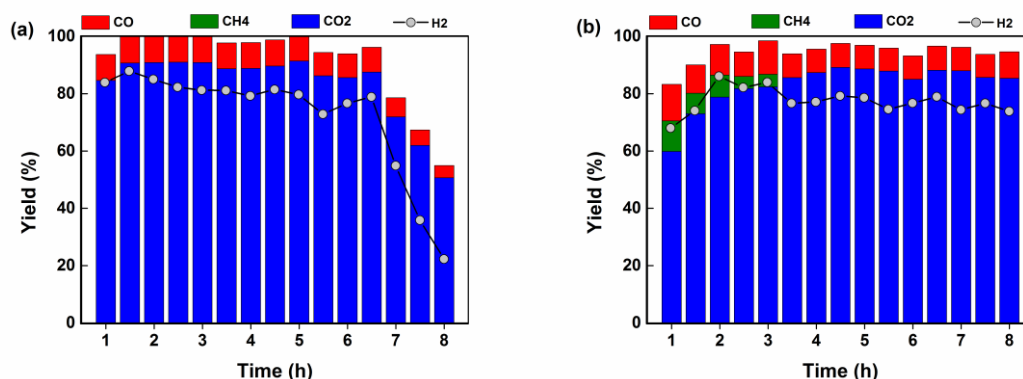


Fig. 7. Protection effect of ZDA: (a) 0.5 g 15 wt.% Ni/ γ -Al₂O₃ catalyst; (b) 0.5 g ZDA plus 0.5 g 15 wt.% Ni/ γ -Al₂O₃ catalyst. T = 700 °C, LHSV = 24 h⁻¹, S/C = 9.2

For 15 wt.% Ni/ γ -Al₂O₃ catalyst plus ZDA (Fig. 7(b)), the performance also started at a high level and reached 100% conversion after approximately 2 h. During the 8-h duration, simulated bio-oil were almost completely converted and the reformation into hydrogen was maintained at a high level. Additionally, through the lifetime test, the output gas composition was almost kept stable with some CO and little CH₄. Considering the total conversion of model compounds, the major contribution of coal ash ZDA was to extend the catalyst lifetime by primarily converting reactants into gaseous productions. After the addition of ZDA, the lifetime was enhanced to at least 8 h, after which the high performance was maintained.

TG Test of Spent Catalysts

The carbon deposition of the spent catalysts was analyzed according to the TG results, as is shown in Table 3. All TG tests were conducted in an air flow (30 mL/min) from ambient temperature to 800 °C at 20 °C/min. The spent catalysts were obtained after 10 h lifetime test at 700 °C, LHSV = 24 h⁻¹, S/C = 9.2. The coke deposition amount was calculated from the weight loss of spent catalysts after TG tests. It can be found that in three Ni/ γ -Al₂O₃ catalysts, the coke deposition was decreased remarkably from 29.2% to 5.3% along with the increase in Ni loading amount. The coke formation could be attributed to the thermal decomposition and numerous side reactions such as oligomerization and cracking (An *et al.* 2011), which would be suppressed at a higher Ni loading amount. After ZDA was introduced above the Ni/ γ -Al₂O₃ catalysts, coke deposition could be further suppressed. It was reported that about 1 wt % coke was generated for one-stage reactor and about 0.4 wt % for two-stage after 3 h test over simulated bio-oil reforming at WHSV at 800 °C, 1 h⁻¹ and S/C = 14. If the present reaction condition was simplified to 1 h test and 1 h⁻¹, the coke amount would be similar to the reported results (Ren *et al.* 2014).

Table 3. Coke Deposition on Ni/ γ -Al₂O₃ Catalysts

Samples	5Ni	5Ni + ZDA	10Ni	10Ni + ZDA	15Ni	15Ni + ZDA
Coke (%)	29.2	26.1	14.5	10.9	5.3	4.8

CONCLUSIONS

1. A selected coal ash was utilized as a guard catalyst and successfully inhibited catalyst deactivation in the catalytic steam reforming of bio-oil for hydrogen production.
2. At a low Ni loading of 5 wt.%, the average carbon conversion was promoted from approximately 30% to more than 60% after the addition of coal ash because it helped to convert reactants into CO and CH₄.
3. When the simulated bio-oil was fully steam-reformed into hydrogen at a high Ni loading of 15 wt.%, the catalyst lifetime was extended from 6 h to at least 8 h with the aid of coal ash.
4. Coke formation on the spent catalysts was also found to be inhibited to a degree, indicating that the coal ash ZDA could not only help reform bio-oil but also prevent the catalyst from becoming deactivated under various conditions.

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